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Product and Method for Protecting Metal During Etching

Field of the Invention

The present invention is directed to a product and process for protecting metals during etching. More specifically, the invention is directed to a product and process for selectively protecting the interior of molds during etching to create a textured surface in unprotected areas of the mold.

Background

Injection molding is widely used to manufacture mass-produced materials. Many injection molds have partially texturized internal surfaces to produce texturized articles. The texture on the internal surfaces can be formed using various methods, and one known method is to mask portions of the internal surfaces that are not to be etched, and then using an acid to etch the non-masked portions. This masking method can result in very precise texturized areas.

Unfortunately, existing methods for masking portions of the internal surfaces of molds have significant limitations. One widely used method involves casting a wax masking material into an etched zinc plate. In this method a zinc plate is coated with a photoresist material, imaged, and developed to make depressions in the plate corresponding to the area to be masked. An acid resist, typically a wax, is deposited into the etched areas and subsequently transferred to a carrier substrate, such as wax paper or rice paper. After the acid resist is transferred to the carrier substrate this substrate is pressed against the interior of a mold and then burnished to transfer the acid resist to the

mold. Unfortunately this method is difficult to perform on large surfaces, image quality can easily be degraded during transfer, placement in the mold is often a challenge with the paper carrier, and even the heat of burnishing can cause some loss of resolution and position of the acid resist.

An alternative method involves directly printing a wax or wax-like acid resist material onto a carrier substrate, such as rice paper, and then transferring this material to the interior of a mold. This method also poses significant problems, including difficulty in positioning the carrier substrate inside a mold, in particular a mold with a curved or complex interior geometry. Also, the heat of burnishing can be a problem, as can be movement of the carrier substrate during transfer of the acid resist material to the substrate.

Yet other methods are known, but these too have problems relating to the ease and accuracy of placement of the resist on the interior of a mold, in particular the interior of irregularly shaped molds. Also, some such methods are time consuming, involving undesirable solvents, or do not provide good, precise masks.

Therefore, a need exists for improved methods and materials for selectively masking portions of an interior of a mold prior to acid etching.

Summary of the Invention

The present invention is directed to a process and product for improved etching of the interior surfaces of molds, in particular for the improved etching of interior surfaces of metal molds, such as molds used in injection molding. The invention permits precise etching of selected areas of the interior of a mold by masking those portions that are not

to be etched. The invention also allows rapid masking without sacrificing quality or precision of placement of the etching mask.

The invention encompasses various implementations. In general the invention involves coating the interior of a mold with a material that will resist etchant. For example, if the etchant is strong acid, then the coating on the interior of the mold should be resistant to strong acids. After the interior of the mold has been coated, parts of the coated area are masked. These masked areas generally correspond to areas of the mold that are not to be etched. Suitable masks include, for example, developed photosensitive films, laser cut adhesive films, manually cut films to which an adhesive has been added, and plastic or rubber stencils configured to be repeatedly used. After the mask has been applied to the interior of the mold, the non-masked portions of the coated interior are removed. In one implementation the non-masked portions of the coating are removed by using an abrasive material, such as abrasive removal with glass beads or sand particles. The mask protects the coating on the interior of the mold so that the non-masked portions are readily removed. Although abrasive removal of the coating is one method of removing the non-masked coating, it will be appreciated that various mechanical and chemical methods may be used. After portions of the etchant resistant coating on the interior of the mold have been removed, an etchant is used to etch the exposed interior mold surface. The etchant is typically an acid, but other materials can also be used.

Having now described general aspects of the invention, more specific embodiments will now be disclosed. In certain implementations a photosensitive film, typically a laminate comprising at least one photosensitive layer containing a photosensitive polymer, is exposed to light of an appropriate wavelength to form a

pattern in the photosensitive layer. The area of the laminate exposed to the light corresponds to the etching pattern in the surface of the mold that will be etched. In some implementations of the invention the exposed pattern is the area that is to be etched, while in other implementations the exposed pattern corresponds to the area of the mold that is to be masked. These distinctions are clarified below with regard to the various implementations of the invention.

In a first implementation of the invention the interior of a mold is coated with an acid-resistant material. A photosensitive laminate is partially exposed to light, with only those areas that are not to be etched being exposed. The laminate is subsequently developed to leave behind that portion of the laminate that has been exposed. Such photosensitive laminates are "negative" laminates, although "positive" laminates can be used that remove the exposed portion of the laminate. The removed portion corresponds to the portion of the mold that is to be etched. After development the laminate is positioned in the interior of the mold over the acid-resistant coating, and then portions of the acid-resistant material are abrasively removed. The laminate is lightly wetted in some implementations in order to make it more flexible and stretchable, thereby allowing it to more readily conform to the interior surface of the mold. The intact portions of the photosensitive laminate (those portions that were not exposed to the light) provide protection to the acid-resist material, while the developed and removed portions of the photosensitive laminate provide little or no protection. Thus, primarily or exclusively those portions the acid-resistant material corresponding to the removed portion of the laminate are removed.

Once the acid-resistant material has been selectively removed the mold is etched with acid, and only those portions of the mold surface that have had the acid-resistant material abrasively removed are exposed to the acid, and therefore only these portions are etched. Excess acid resistant material is typically removed after etching, as well as any remaining photosensitive laminate.

The above summary of the present invention is not intended to describe each disclosed embodiment of the present invention. This is the purpose of the figures and the detailed description that follow.

Figures

Other aspects and advantages of the invention will become apparent upon reading the following detailed description and upon reference to the drawing in which:

Figure 1 is a simplified perspective view of a mold constructed and arranged in accordance with the invention.

Figure 2 is a side cross-sectional view of the mold of Figure 1, the cross section taken along lines A-A' of Figure 1.

Figure 3 is an enlarged cross-sectional view of the mold of Figures 1 and 2, the enlarged cross section taken between points B and B' of Figure 2, showing etched and non-etched areas of the mold

Figure 4 is an enlarged cross-sectional view of the mold of Figure 3, showing the mold prior to being etched but after having been coated with an acid resistant material.

Figure 5 is an enlarged cross-sectional view of the mold of Figure 4, showing the mold after a developed photosensitive film has been applied to the acid resistant material.

Figure 6 is an enlarged cross-sectional view of the mold of Figure 5, showing the mold after abrasive removal of excess acid resistant material.

Figure 7 is an enlarged cross-sectional view of the mold of Figure 5, showing the mold after acid etching of the mold and removal of remaining acid resistant material.

While the invention is susceptible to various modifications and alternative forms, specifics thereof have been shown by way of example in the figure and will be described in detail. It should be understood, however, that the intention is not to limit the invention to the particular embodiments described. On the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.

Detailed Description

The present invention is directed, in general, to coating the interior of a mold with a material that will resist etchant, and then selectively removing the etchant to create a desirable pattern in the mold. If the etchant is strong acid, then the etchant-resistnat coating on the interior of the mold should be resistant to strong acids. After the interior of the mold has been coated, parts of the coated area are masked. These masked areas generally correspond to areas of the mold that are not to be etched.

Suitable masks include, for example, developed photosensitive films, laser cut adhesive films, manually cut films to which an adhesive has been added, printed abrasive resistant material (printed by inkjet, screen printing, etc.) and plastic or rubber stencils configured to be repeatedly used. After the mask has been applied to the interior of the mold, the non-masked portions of the coated interior are removed.

In one implementation the non-masked portions of the coating are removed by using an abrasive material, such as abrasive removal with glass beads or sand particles. The mask protects the coating on the interior of the mold so that the non-masked portions are readily removed. Although abrasive removal of the coating is one method of removing the non-masked coating, it will be appreciated that various mechanical and chemical methods may be used.

After portions of the etchant resistant coating on the interior of the mold have been removed, an etchant is used to etch the exposed interior mold surface. The etchant is typically an acid, but other materials can also be used.

The present invention can more easily be understood by reference to the figures, which will now be described in greater detail. In Figure 1 a simplified perspective view of a mold 10 constructed and arranged in accordance with the invention is shown. Mold 10 has a cavity 12 with an interior surface 14 surrounded by a wall 16, which is typically formed of metal or another acid-etchable material.

Figure 2 shows a side cross-sectional view of the mold 10 of Figure 1, the cross section taken along lines A-A' of Figure 1. The cavity 12 of mold 10 includes the interior surface 14, part of which is typically etched to create a texture in accordance with the present invention. The mold 10 shown in Figures 1 and 2 is depicted only to show general aspects of a mold suitable for use with the various embodiments of the invention, and is does not show many of the intricacies and additional features that are common in molds. However, one aspect of the mold 10 shown in Figure 2 is the curved interior surface 14 of cavity 12. Many molds have complex internal geometries with curves,

bends, and sharp angles. It is desirable to have a method and materials that permits etching within these complex surfaces with precision and efficiency.

Figure 3 is an enlarged cross-sectional view of the mold 10 of Figures 1 and 2, the enlarged cross section taken between points B and B' of Figure 2, showing non-etched areas 18 and etched areas 20 interior surface 14. Again, these non-etched and etched areas 18, 20 are shown for illustrative purposes. The non-etched and etched areas 18 and 20 can be varied to form unlimited patterns and arrangements. These areas are shown here in a very simplified form, but it should be appreciated that they can take on many different shapes.

Figure 4 is an enlarged cross-sectional view of the mold 10 of Figure 3, showing the mold 10 prior to being etched but after having been coated with an acid resistant material 22 in accordance with the teaching of a first implementation of the invention. Suitable acid resistant materials include, for example, spray applied lacquers, enamels, etc. The acid resistant material 22 is generally a thin layer that has strong resistance to acids, but is typically readily removed from the mold 10 after the acid etching process has been completed. The acid resistant material is typically applied as a liquid that subsequently dries or hardens. However, in some implementations the acid resistant material can be applied as a sheet, such as a polymeric film applied and secured to the interior surface 14 of the mold 10 using a pressure sensitive adhesive. Acid resistant materials applied as a liquid are generally advantageous over sheet materials because the liquid more readily conforms to complex geometries. The acid resistant material is typically removable by abrasives, such as blasting with glass beads or sand particles.

In this first implementation of the invention the acid resistant material 22 (typically after drying or hardening, when applied as a liquid) is covered with a developed photosensitive film 30 (as shown in Figure 5). This photosensitive film 30 contains, for example, a carrier film 32 and a developed polymeric layer 34. The developed polymeric layer 34 contains areas 36 that are intact and provide protection against abrasive etching, along with areas 38 that have been removed or degraded and do not provide protection against abrasive etching. Thus, Figure 5 is an enlarged cross-sectional view of the mold of Figure 4, showing the mold after a developed photosensitive film 30 has been applied to the acid resistant material. The purpose of this developed photosensitive film 30 is to provide protection for parts of acid resistant material 22. Those portions of the acid resist material 22 that are protected against abrasive etching are not readily removed by sand blasting or bead blasting, and thus remain in place to protect the underlying mold surface from acid etching. In contrast, those portions of the acid resist material 22 that are not protected against abrasive etching are readily removed or degraded during sand blasting or bead blasting, and do not protect the underlying mold surface from acid etching.

It will be appreciated that some or all of the photosensitive film 30 and the non-removed acid resist material 22 can be left in place during etching in some implementations of the invention, while in other implementations all of the photosensitive film 30 is removed (such as by using a solvent bath) before etching of the interior of the mold.

In some implementations it is desirable to lightly wet the photosensitive film 30 during placement in the interior of the mold 10. The wetting allows the photosensitive

film to become more conformable and elastic, thereby improving the ease and precision at which it can be placed. Moisture is typically absorbed by a membrane layer that retains the developed photosensitive film. Suitable membrane layers include, for example, hydrolyzed polyvinyl alcohols. Suitable wetting agents include water, as well as water mixed with glycols, such as glycerols. In a first embodiment pure water is used, while in a second embodiment from 10 to 30 percent glycerol is added. The glycerol promotes stretching of the film, in particular the memberane, even after the volatile water has evaporated. Typically the wetting agent is less than 50 percent of the glycol, but in certain embodiments even more than 50 percent of glycol is mixed with water. Although less preferred, other wetting agents can be used. For example, organic solvents are suitable with some membranes, although water based mixtures are more desirable.

Figure 6 is an enlarged cross-sectional view of the mold of Figure 5, showing the mold after abrasive removal of excess acid resistant material. A portion of the acid resistant material 22 and a portion of the photosensitive film 30 remain on top of the interior surface 14 of mold 10, but other areas that were not protected by photosensitive film 30 are free of acid resistant material 22. The mold 10 is subsequently etched with a strong acid, leaving an etched surface corresponding to that of Figure 7, showing the mold 10 after acid etching of the mold and removal of remaining acid resistant material and any remaining photosensitive film 30.

It is possible to repeat the method of the invention multiple times (generally no more than 10 times, but more than 10 in some implementations, and more commonly less than 5 times). The repetition of the method involves repeating the coating, masking, etching process multiple times so that complex etches can be created. The present

invention is particularly suitable to creation of complex forms because the etchant-resistant coating of the invention readily coats exposed etched surfaces, thereby giving greater control to subsequent etching steps.

Aspects of the photosensitive laminate will now be described in greater detail. The photosensitive laminate generally includes a carrier layer that holds the other layers prior to their being placed on a substrate. Thus, the photosensitive laminate structure usually contains at least one photosensitive layer and a carrier layer. A membrane layer may also be included and is placed between the carrier and photosensitive layers. Additional layers can be included without deviating from the scope and intent of the invention, including layers placed between the layers discussed herein as long as they do not eliminate the functionality described herein.

In certain implementations the photosensitive laminate contains at least two photosensitive layers, including a first tacky photosensitive layer and a second substantially non-tacky photosensitive layer. The tacky photosensitive layer provides adhesion to a substrate, such as a substrate that is to be etched. The photosensitive layer comprises a pressure sensitive adhesive composition having a T_g of less than about -40° C.

Suitable photosensitive resist layers made in accordance with the invention are described below as examples.

Example Photosensitive Layer I

Material	Wt %
polyvinyl acetate copolymer pressure sensitive adhesive [1]	44.9
polyvinyl alcohol grafted with SBQ [2]	19.1
water	15.8
plasticizers, benzoate esters [3]	14.4
glycerin	5.1
Zonyl FSO, fluorosurfactant	0.7
Keyamine violet KB 220%, disazo dye	0.04

[1] Flexbond 150, available from Air Products, Allentown, PA. Alternatively, a UV-curable pressure sensitive adhesive (PSA) can be used, or a mixture of a UV-curable and non-UV- curable PSAs can be used.

[2] PVA-SBQ available from Toyo Gosei, Japan.

[3] Benzoflex 50, available from Velsicol Chemical Co., Rosemont, IL.

Example Photosensitive Layer II

Material	Wt %
UV-curable pressure sensitive adhesive[1]	15
polyvinyl acetate copolymer pressure sensitive adhesive	15.36
plasticizers, benzoate esters	14.56
glycerin	5.1
polyvinyl acetate, resin emulsion in water	15
Unisperse Blue G-EN, phthalocyaninato pigment	0.3
Zonyl FSO, fluorosurfactant	0.67
water	17.63
polyvinyl alcohol grafted with SBQ	16.38

[1] Rad-Bond 12PSF5K, available from RAD-CURE Corporation, Fairfield, NJ

Example Photosensitive Layer III

Material	Wt %
polyvinyl acetate, resin emulsion in water [1]	38.19
polyvinyl alcohol grafted with SBQ [2]	30.07
polyvinyl acetate homopolymer [3]	8.19
vinyl acetate/ethylene copolymer [4]	8.19
plasticizer, benzoate esters [5]	7.50
water	3.06
glycerin	2.91
isopropyl alcohol	1.56
Unisperse Blue G-EN, phthalocyaninato pigment	0.20
Zonyl FSO, fluorosurfactant	0.11

[1] PN-3178Z, available from H.B. Fuller Company, St. Paul, MN.

[2] 540-SBQ, available from Toyo Gosel, Japan.

[3] XR-2223, available from H.B. Fuller Company, St. Paul, MN.

[4] AF-320, available from Air Products, Allentown, PA.

[5] Benzoflex 50, available from Velsicol Chemical Co., Rosemont, IL.

Example Photosensitive Layer IV

Material	Wt %
polyvinyl acetate, resin emulsion in water [1]	46.53
polyvinyl alcohol grafted with SBQ [2]	17.98
polyvinyl acetate homopolymer [3]	10.52
vinyl acetate/ethylene copolymer [4]	10.52
plasticizer, benzoate esters [5]	5.0
water	3.75
glycerin	3.30
isopropyl alcohol	2.07
Unisperse Blue G-EN, phthalocyaninato pigment	0.21
Zonyl FSO, fluorosurfactant	0.12

[1] PN-3178Z, available from H.B. Fuller Company, St. Paul, MN.

[2] 540-SBQ, available from Toyo Gosel, Japan.

[3] XR-2223, available from H.B. Fuller Company, St. Paul, MN.

[4] AF-320, available from Air Products, Allentown, PA.

[5] Benzoflex 50, available from Velsicol Chemical Co., Rosemont, IL.

The photosensitive laminate also usually contains a carrier layer. The carrier layer allows easy transport and positioning of the laminate film prior to placement in a mold while also providing support to the other laminate layers. Typically the carrier layer remains on the photosensitive laminate until just before application of the abrasive media. The carrier layer can contain, for example, polyester, biaxially oriented

polypropylene, high density polyethylene, low density polyethylene, or other polymer films.

The photosensitive laminate structure also normally contains a membrane layer. Generally the membrane layer functions as both an anchoring layer to secure the carrier layer to the photosensitive layer, as well as a release layer or release liner between the carrier layer and photosensitive layer. Suitable membrane layers include, for example, polyvinyl alcohols, polyvinyl butyral, polyvinyl formal, polyurethane, nitrocellulose, a polyvinyl pyrrolidone copolymer, and urethane acrylic polymers. As discussed earlier in this description, the membrane layer serves to secure and retain the photosensitive layer after it has been developed and the carrier layer has been removed. In general the membrane is quite thin, and is preferably stretchable. This stretchability can be enhanced by wetting the membrane, such as by wetting with a water based solution containing glycerin. Stretchability is advantageous because it allows the film to be conformed to the interior of curved mold surfaces without folding or cutting. However, the film should not be so stretchable that it easily loses its shape. Typically the film is readily stretchable by at least 10 percent, and generally stretchable by up to and exceeding 25 percent when a moderate force is applied, and after being lightly wetted. Regardless of the quantitative stretchability of the film and membrane, it is qualitatively significantly more stretchable than celluse papers and Myler® films, neither of which show good stretchability. The membrane can be of any thickness that allows proper placing of the photosensitive layer. In most implementations the membrane is less than 25 microns thick, more typically less than 10 microns thick, and even more typically less than 5 microns thick. In some

embodiments the membrane is 3 to 5 microns thick, while in other embodiments it is from 2 to 7 microns thick.

In addition to being stretchable, the film can advantageously be configured so that it is repositionable. Thus, the film can gently be pulled back from the surface of the mold and moved if necessary before etching of the acid resistant material. Such repositionability is possible by using a photosensitive layer that has moderate tackiness, or by coating the photosensitive layer with a pressure sensitive adhesive that is sufficient to adequately hold the photosensitive layer in place during abrasive removal of the acid resist, yet readily releases from the acid resist surface to reposition the photosensitive layer or to remove the photosensitive layer after the abrasive removal of the acid resist.

Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a full scope and spirit of the invention being indicated by the following claims.